

**LARSON & TAYLOR, PLC** • 1199 North Fairfax St. • Suite 900 • Alexandria, VA 22314

U.S. APPLICATION NO. <b>09/700185</b>		INTERNATIONAL APPLICATION NO. PCT/JP99/02398		ATTORNEY DOCKET NO. P06971US00/LRP											
<input checked="" type="checkbox"/> 17. The following fees are submitted: <input checked="" type="checkbox"/> <b>Basic National Fee</b> (37 CFR 1.492 (a) (1)-(5): <table border="0"> <tr> <td><input type="checkbox"/> Neither Int'l Prelim. Exam. fee nor Int'l Search fee paid to USPTO</td> <td>\$1000</td> </tr> <tr> <td><input checked="" type="checkbox"/> Search Report has been prepared by the EPO or JPO</td> <td>\$ 860</td> </tr> <tr> <td><input type="checkbox"/> No Int'l Prelim. Ex. fee paid to USPTO but Int'l Search fee paid to USPTO</td> <td>\$ 710</td> </tr> <tr> <td><input type="checkbox"/> International preliminary examination fee paid to USPTO</td> <td>\$ 690</td> </tr> <tr> <td><input type="checkbox"/> Int'l Prelim. Ex. fee paid to USPTO &amp; all claims satisfied PCT Art. 33(1)-(4)</td> <td>\$ 100</td> </tr> </table>				<input type="checkbox"/> Neither Int'l Prelim. Exam. fee nor Int'l Search fee paid to USPTO	\$1000	<input checked="" type="checkbox"/> Search Report has been prepared by the EPO or JPO	\$ 860	<input type="checkbox"/> No Int'l Prelim. Ex. fee paid to USPTO but Int'l Search fee paid to USPTO	\$ 710	<input type="checkbox"/> International preliminary examination fee paid to USPTO	\$ 690	<input type="checkbox"/> Int'l Prelim. Ex. fee paid to USPTO & all claims satisfied PCT Art. 33(1)-(4)	\$ 100	CALCULATIONS PTO USE ONLY	
<input type="checkbox"/> Neither Int'l Prelim. Exam. fee nor Int'l Search fee paid to USPTO	\$1000														
<input checked="" type="checkbox"/> Search Report has been prepared by the EPO or JPO	\$ 860														
<input type="checkbox"/> No Int'l Prelim. Ex. fee paid to USPTO but Int'l Search fee paid to USPTO	\$ 710														
<input type="checkbox"/> International preliminary examination fee paid to USPTO	\$ 690														
<input type="checkbox"/> Int'l Prelim. Ex. fee paid to USPTO & all claims satisfied PCT Art. 33(1)-(4)	\$ 100														
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$860											
<input type="checkbox"/> Surcharge of \$130 for furnishing the oath or declaration later than from the earliest claimed priority date (37 CFR 1.492(e)). <table border="0"> <tr> <td><input type="checkbox"/> 20 mos.</td> <td></td> </tr> <tr> <td><input type="checkbox"/> 30 mos. +</td> <td>\$</td> </tr> </table>				<input type="checkbox"/> 20 mos.		<input type="checkbox"/> 30 mos. +	\$								
<input type="checkbox"/> 20 mos.															
<input type="checkbox"/> 30 mos. +	\$														
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE												
Total Claims	- 20 =		X \$18 =	\$											
Independent Claims	- 03 =		X \$80 =	\$											
<input type="checkbox"/> Multiple Dependent Claim(s) (if applicable)			+ \$270 =	\$											
TOTAL OF ABOVE CALCULATIONS =				\$ 860											
<input type="checkbox"/> Reduction of 1/2 for small entity status of applicant.				\$											
SUBTOTAL =				\$ 860											
<input type="checkbox"/> Processing fee of \$130 for furnishing the English translation later than from the earliest claimed priority date (37 CFR 1.492(f)). <table border="0"> <tr> <td><input type="checkbox"/> 20 mos.</td> <td></td> </tr> <tr> <td><input type="checkbox"/> 30 mos. +</td> <td>\$</td> </tr> </table>				<input type="checkbox"/> 20 mos.		<input type="checkbox"/> 30 mos. +	\$								
<input type="checkbox"/> 20 mos.															
<input type="checkbox"/> 30 mos. +	\$														
TOTAL NATIONAL FEE =				\$ 860											
<input checked="" type="checkbox"/> Fee for recording the enclosed assignment, accompanied by a cover sheet - \$40 per property				\$ 40											
TOTAL FEES ENCLOSED =				\$ 900											
Amount to be				Refunded	\$										
				Charged	\$										
<input checked="" type="checkbox"/> a. A check in the amount of \$900 to cover the above fees is enclosed. <input type="checkbox"/> b. Please charge my Deposit Account No. 12-0555 in the amount of \$ to cover the above fees. <input checked="" type="checkbox"/> c. The Commissioner is hereby authorized to charge any additional fees required or credit overpayment to Deposit Account No. 12-0555.															
<b>Note:</b> Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.															
SEND ALL CORRESPONDENCE TO:			SIGNATURE: <u>Douglas E. Jackson</u>												
LINDA R. POTEATE			NAME: DOUGLAS E. JACKSON												
At the address (below) of CUSTOMER NO. 000881.			REG. NO.: 28518												
LARSON & TAYLOR, PLC			PHONE NO.: 703-739-4900												
1199 NORTH FAIRFAX ST.			Date: 13 NOVEMBER 2000												
SUITE 900															
ALEXANDRIA, VA 22314															

003121 "EST 00460

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Patent

In re patent application of: ARAKI, et al

Serial No.: 09/700,185

Examiner:

Filed: November 13, 2000

Art Unit:

For: MATERIAL FOR SOLID POLYELECTROLYTE  
SUITABLE FOR USE IN FUEL CELL

Docket No.: P06971US00/LRP

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, D.C.

S I R:

Prior to examination, please amend the above-identified application as follows:

**IN THE SPECIFICATION:**

Please amend the specification as follows:

Page 9, line 7, change “(CF<sub>2</sub>CF(CF<sub>3</sub>O)<sub>m1</sub>” to --(CF<sub>2</sub>CF(CF<sub>3</sub>O)<sub>m1</sub>--; and

line 8, change “(CF<sub>2</sub>O(CF<sub>2</sub>CF<sub>2</sub>O)<sub>m5</sub>” to --CF<sub>2</sub>O(CF<sub>2</sub>CF<sub>2</sub>O)<sub>m5</sub>--.

**IN THE CLAIMS:**

Please amend claims 2, 5, 8, 12 and 14 as follows:

Claim 2, lines 1-2, change “which comprises” to --comprising--;

Claim 5, line 3, change “is” to --comprises”;

Claim 8, lines 1-2, change “which comprises” to --comprising--;

Claim 12, line 1, change “which is” to --comprising--; and

Claim 14, lines 2-3, delete “or 8”.

003721 53700460

Please add new claim 29 as follows:

--29. A solid polyelectrolyte membrane comprising the multi-segmented fluoropolymer according to claim 8.--

REMARKS

The foregoing amendment is being submitted to correct typographical errors which appear in the English translation being submitted concurrently herewith and to correct various informalities in the claims and eliminate multiple dependencies. Attached hereto is a copy of page 5 of the published PCT application which is in Japanese in support of this amendment.

Favorable consideration is respectfully requested.

Respectfully submitted,

LARSON & TAYLOR, PLC



Linda R. Poteate

Registration No. 36255

1199 North Fairfax Street, Suite 900  
Alexandria, Virginia 22314  
(703) 739-4900

December 18, 2000

00312153700250

ルキレン基、エーテル結合を有する2価の含フッ素アルキレン基であり、より好ましくは水素を含まないハロゲン原子のみから構成される2価の含フッ素アルキレン基、エーテル結合を有する2価の含フッ素アルキレン基であり、特にフッ素原子のみから構成されるものが好ましい。

炭素数1～40の2価の含フッ素アルキレン基としては、 $-(CF_2)_m-$ ;  
 $-(CF_2CF(CF_3))_{m1}-$ ;  $-(CF(CF_3)CF_2)_{m1}-$ ;  
 $-(CF_2CFCI)_{m2}-$ ;  $-(CF_2CH_2)_{m2}-$ ;  
 $-(CF_2)_{m3}-(CF_2)_{m4}-$ ;  $-(CF_2CF(CFCI_2))_{m1}-$ ;

[式中、mは1～40の整数、m1は1～13の整数、m2は1～20の整数、 $m3 \geq 1$ 、 $m4 \geq 1$  かつ  $1 \leq m3 + m4 \leq 40$ ]

が例示される。

炭素数1～40のエーテル結合を有する2価の含フッ素アルキレン基としては、  
 $-(CF_2CF_2O)_{m2}-$ ;  $-(CF_2CF(CF_3)O)_{m1}-$ ;  
 $-(CF_2CF_2CF_2O)_{m1}-$ ;  $-(CF_2CF_2CH_2O)_{m1}-$ ;  
 $-CF_2O(CF_2CF(CF_3)O)_{m1}-$ ;  $-CF_2O(CF_2CF_2O)_{m5}-$ ;  
 $-(CF_2CF(CFCI_2)O)_{m1}-$ ;

[式中、m1およびm2は前記に同じ。m5は1～19の整数]  
 が例示される。

つまり、本発明の固体高分子電解質に用いられる含フッ素多元セグメント化ポリマーは、イオン伝導性機能を有するスルホン酸型官能基含有する含フッ素ポリマー鎖セグメント(セグメントA)と、ポリマー全体に機械的強度、耐久性を与え得る含フッ素ポリマー鎖セグメント(セグメントB)を含む含フッ素セグメント化ポリマーであり、ポリマー全体に機械的強度を向上させるためには、含フッ素ポリマー鎖セグメントBは、結晶性を有するポリマー鎖、または非晶性であってもガラス転移点が高いポリマー鎖が好ましく、具体的には、結晶融点またはガラス転移点が100℃以上、特に好ましくは200℃以上の含フッ素ポリマー鎖セグメント(セグメントB)を有するものが好ましい。

あるいは、イオン伝導性機能がより高いスルホン酸型官能基の含量の高い(当量数の小さい)含フッ素ポリマー鎖セグメント(セグメントC)と、機械的強度、

-1-

DESCRIPTION

MATERIAL FOR SOLID POLYELECTROLYTE

SUITABLE FOR USE IN FUEL CELL

TECHNICAL FIELD

5           The present invention relates to fluoropolymer materials suitable for solid polyelectrolytes, and solid polyelectrolyte membranes comprising the materials.

BACKGROUND ART

10           Fuel cells are electrochemical devices that convert chemical energy directly into electrical energy by oxidization of fuel supplied to the cells. Generally, a fuel cell comprises two gas diffusion electrodes adjacent to and in contact with an electrolyte, and includes a means for supplying fuel to the positive electrode and  
15           supplying an oxidant to the negative electrode. The electrolyte, either solid or liquid, is located between the electrodes and transfers ions between the positive and negative electrodes.

20           One type of fuel cell utilizes a proton exchange polymer film as the electrolyte. In this type of fuel cell, a plurality of acid functional groups chemically bonded to the polymer main chain of the polymer film have an electrolytic action. The proton exchange polymer film may be made of, for example, sulfonated polystyrene, or  
25           preferably a substantially fluorinated sulfonic acid

005121 52100250

polymer such as a Nafion ion exchange polymer film manufactured by Du pont. The term "solid polyelectrolyte" is often used to indicate any of these ion exchange polymer film structures.

- 5                   Proton exchange polymer film fuel cells are known, and disclosed in, for example, U.S. Patent No. 3134697. Early solid polyelectrolyte proton exchange polymer film fuel cells were operable, but had a limited life because of the chemical instability of the polymer
- 10 film as such. However, subsequently developed perfluorinated polymer materials having ion exchange activity, such as Nafion manufactured by Du pont, enabled provision of fuel cells of the above type which have good operation properties and a several thousand hour life.
- 15                   A solid polyelectrolyte fuel cell comprising Nafion (perfluorosulfonic acid polymer film) is operated generally at about 80°C. Since the polymer film as such is substantially gas-impermeable, the cell does not necessitate any porous support matrix for preventing
- 20 mixing of gases, which is usually employed when using a liquid electrolyte fuel cell. By using a suitable external support, a pressure difference of 100 psi or more can be provided between the fuel gas and oxidant gas in practical operation. These characteristics are remarkably
- 25 advantageous. When the fuel cell is operated using, as an

09700185 121300

oxidant, air with an increased pressure to raise the oxygen partial pressure, compression of the fuel gas becomes unnecessary. For example, a hydrogen/air fuel cell can be operated using fuel at 1 atmosphere and air  
5 (oxidant) at 4 atmospheres or more.

In practice, the electrodes are physically bonded to the active proton exchange polymer film by application of pressure or heat (e.g., U.S. Patent No. 4272353).

10 In the present state of the art,  
perfluorosulfonic acid polymer films manufactured by Du pont, as described in U.S. Patent No. 3282875, are used as films having an equivalent weight of about 1100 to 1200. Equivalent weight means the weight of a polymer necessary  
15 for neutralizing 1 equivalent of a base. It is presumed that the ion conductivity of a polymer film is in inverse proportion to the equivalent weight of the polymer film. There is a film of Nafion ion exchange polymer having a lower equivalent weight than the polymer film  
20 conventionally employed in the art (EP Patent Application No. 0122049). However, polymer films having an equivalent weight less than about 950 have low physical stability as described in "Dual Cohesive Energy Densities of Perfluoro-  
sulphonic Acid (Nafion) Membrane" (Polymer, vol. 21, pp. .  
25 432-435, April, 1980). Thus, such polymer films have



handling difficulties during assembling of a cell unit, or produce creep during assembling or operation of a cell, thus causing voltage loss or short circuit and losing reliability. A proton exchange solid polyelectrolyte with  
5 a reduced equivalent weight is strongly desired in order to decrease the resistance loss of ion transfer in fuel cells while maintaining acceptable properties of the cells.

A variety of attempts have been made to solve the problems of solid polyelectrolyte films.

10 For example, International Patent Application Translation Publication No. 1987-500759 states that the structure of the Nafion ion exchange polymer having sulfonic acid groups in the polymer side chain is modified, i.e., the sulfonic acid group-containing side chain  
15 structure is made shorter. As a result, according to the publication, the polymer has a lower equivalent weight (less than 1000) and an improved storage elastic modulus at a high temperature (110°C or higher). In this  
20 technique, the glass transition point or softening point of the Nafion ion exchange polymer (about 110°C) is raised to improve the high-temperature mechanical properties. However, sulfonic acid group-containing polymers, including Nafion ion exchange polymers, are intrinsically amorphous or have an extremely low crystallinity even if  
25 they have a crystalline moiety. Therefore, these

polymers are insufficient in mechanical properties at room temperature or high temperatures.

Further, it is very difficult to synthesize the disclosed sulfonic acid group-containing polymers whose  
5 sulfonic acid group-containing side chain is short.  
Therefore, such polymers are disadvantageous in productivity and cost.

Japanese Unexamined Patent Publication No. 1994-231778 discloses a blend of at least two perfluorocarbon  
10 polymers having sulfonic acid groups, which polymers are different in ion exchange capacity, for use in a solid polyelectrolyte fuel cell. According to the publication, the blend has high ion exchange capacity and contributes to high mechanical strength.

15 However, the publication discloses a mere blend of a perfluorocarbon polymer having a large amount of sulfonic acid group-containing units and a perfluorocarbon polymer having a small amount of sulfonic acid group-containing monomer units. Therefore, the mechanical  
20 strength of the blend is middle between the mechanical strengths of the unblended polymers. Moreover, the polymer with low ion exchange capacity (with small sulfonic acid group content), which contributes to the mechanical strength, do not have significantly high  
25 mechanical properties, and thus is not capable of giving

the blend sufficient mechanical strength. Furthermore, it is difficult to homogeneously blend the polymers, thus resulting in impaired proton transfer properties.

Japanese Unexamined Patent Publication No. 1994-

5 231781 describes a solid polyelectrolyte fuel cell comprising a laminate of at least two perfluorocarbon polymers containing sulfonic acid groups, which polymers are different in water content. In this technique, the perfluorocarbon polymer with a low water content (with a  
10 small amount of sulfonic acid group-containing monomer units) in the laminate is intended to contribute to high mechanical strength. However, the low water-content polymer as such has insufficient mechanical strength, and the layer of the polymer is thin, and therefore the  
15 laminate does not have sufficiently improved mechanical strength. Moreover, the laminated layers have a high water-content portion, and a low water-content having low ion transfer properties. Thus, the laminate as a whole has reduced proton transfer properties.

20 The present invention has been accomplished in view of the above problems of the prior art.

An object of the present invention is to provide a solid polyelectrolyte material having necessary and sufficient hydrogen ion conductivity (ion exchange group  
25 concentration) for use in a fuel cell comprising a

09700185-121800

5

Fig. 1 is a conceptual view showing a polymer having a segmented polymer chain A and a segmented polymer chain B.

10

## 15

20

25

The solid polyelectrolyte material of the

invention comprises a multi-segmented fluoropolymer having at least two types of fluoropolymer chain segments differing in composition of monomers forming the polymers, at least one type of the fluoropolymer chain segments  
5 containing sulfonic acid functional groups capable of imparting ion conductivity.

As used herein, the term "sulfonic acid functional group" means  $\text{SO}_3\text{M}$  (wherein M is hydrogen, an alkali metal salt, an alkaline earth metal salt, or an  
10 ammonium cation wherein a proton is added to ammonia, primary amine, secondary amine or tertiary amine),  $\text{SO}_2\text{Cl}$  or  $\text{SO}_2\text{F}$ . Preferred sulfonic acid functional groups are  $\text{SO}_3\text{H}$ ,  $\text{SO}_2\text{Cl}$  and  $\text{SO}_2\text{F}$ .

Rf represents a  $\text{C}_1$  to  $\text{C}_{40}$  divalent fluoroalkylene  
15 group or a  $\text{C}_1$  to  $\text{C}_{40}$  divalent fluoroalkylene group having ether bond(s); preferably a divalent fluoroalkylene group or a divalent fluoroalkylene group having ether bond(s), which consists solely of fluorine atom(s), hydrogen atom(s) or halogen atom(s) other than fluorine; more  
20 preferably a divalent fluoroalkylene group or a divalent fluoroalkylene group having ether bond(s), which is free from hydrogen and consists solely of halogen atom(s), particularly fluorine atom(s).

Examples of  $\text{C}_1$ - $\text{C}_{40}$  divalent fluoroalkylene groups  
25 include  $-(\text{CF}_2)_m-$ ;  $-(\text{CF}_2\text{CF}(\text{CF}_3))_{m1}-$ ;  $-(\text{CF}(\text{CF}_3)\text{CF}_2)_{m1}-$ ;

$-(\text{CF}_2\text{CFCl})_{m2}-$ ;  $-(\text{CF}_2\text{CH}_2)_{m2}-$ ;  $-(\text{CF}_2)_{m3}-(\text{CF}_2)_{m4}-$  and  
 $-(\text{CF}_2\text{CF}(\text{CFCl}_2))_{m1}-$  [wherein  $m$  is an integer of 1 to 40,  $m1$   
is an integer of 1 to 13,  $m2$  is an integer of 1 to 20,  
 $m3 \geq 1$ ,  $m4 \geq 1$  and  $1 \leq m3+m4 \leq 40$ ].

5                Examples of  $\text{C}_1\text{-C}_{40}$  divalent fluoroalkylene groups  
having ether bond(s) include  $-(\text{CF}_2\text{CF}_2\text{O})_{m2}-$ ;  
 $-(\text{CF}_2\text{CF}(\text{CF}_3\text{O}))_{m1}-$ ;  $-(\text{CF}_2\text{CF}_2\text{CF}_2\text{O})_{m1}-$ ;  $-(\text{CF}_2\text{CF}_2\text{CH}_2\text{O})_{m1}-$ ;  
 $-\text{CF}_2\text{O}(\text{CF}_2\text{CF}(\text{CF}_3)\text{O})_{m1}-$ ;  $-(\text{CF}_2\text{O}(\text{CF}_2\text{CF}_2\text{O}))_{m5}-$  and  
10  $-(\text{CF}_2\text{CF}(\text{CFCl}_2)\text{O})_{m1}-$  [wherein  $m1$  and  $m2$  are as defined above,  
and  $m5$  is an integer of 1 to 19].

              The multi-segmented fluoropolymer for use in the  
solid polyelectrolyte according to the invention comprises  
a fluoropolymer chain segment containing sulfonic acid  
functional groups and having ion conductivity (Segment A)  
15 and a fluoropolymer chain segment capable of imparting  
mechanical strength and durability to the whole polymer  
(Segment B). For improving the mechanical strength of the  
whole polymer, it is preferable that the fluoropolymer  
chain segment B is a crystalline polymer chain, or an  
20 amorphous polymer chain having a high glass transition  
point. Specifically stated, the multi-segmented  
fluoropolymer preferably has a fluoropolymer chain segment  
(Segment B) having a crystalline melting point or glass  
transition point of  $100^\circ\text{C}$  or higher, more preferably  $200^\circ\text{C}$   
25 or higher.

Alternatively, the segmented fluoropolymer according to the invention may comprise a fluoropolymer chain segment having higher ion conductivity because of its high sulfonic acid functional group content (a small equivalent weight) (Segment C) and a fluoropolymer chain segment having higher mechanical strength and durability (Segment D).

Also in this case, the fluoropolymer chain segment D is preferably a crystalline polymer chain or an amorphous polymer chain having a high glass transition point. Specifically stated, Segment D is a polymer chain segment having a crystalline melting point or glass transition point of 100°C or higher, more preferably 200°C or higher.

It is essential that the multi-segmented fluoropolymer for use in the solid polyelectrolyte material of the invention be a fluoropolymer comprising, in one molecule, a fluoropolymer chain segment containing sulfonic acid functional groups (Segment A) and a fluoropolymer chain segment containing no sulfonic acid functional groups (Segment B), Segments A and B being combined in the form of blocks or a graft; or a fluoropolymer comprising, in one molecule, a fluoropolymer chain segment with a higher sulfonic acid functional group content (Segment C) and a fluoropolymer chain segment with

a lower sulfonic acid functional group content (Segment D), Segments C and D being combined in the form of blocks or a graft.

In the present invention, a variety of known processes can be employed to combine Segment A with Segment B, or Segment C with Segment D in the form of blocks or a graft to obtain a multi-segmented fluoropolymer. Among these processes, preferred are a process for preparing a multi-segmented block fluoropolymer disclosed in Japanese Examined Patent Publication No. 1983-4728 and other publications; and a process for preparing a multi-segmented graft fluoropolymer disclosed in Japanese Unexamined Patent Publication No. 1987-34324.

Particularly preferred is a multi-segmented block fluoropolymer prepared by the so-called iodine transfer polymerization process described in Japanese Examined Patent Publication No. 1983-4728 and Kobunshi Ronbunshu (Japanese Journal of Polymer Science and Technology, Vol. 49, No. 10, 1992).

Generally, a mere blend of a sulfonic acid functional group-containing fluoropolymer (a homopolymer corresponding to Segment A) and a fluoropolymer having higher mechanical properties than the sulfonic acid functional group-containing fluoropolymer (a homopolymer



corresponding to Segment B) is insufficient in mechanical properties, or has reduced ion conductivity, although depending on the kinds, miscibility, compatibility and like characteristics of the polymers in the blend.

5           In contrast, the multi-segmented polymer according to the present invention is obtained by combining a sulfonic acid functional group-containing fluoropolymer chain segment (Segment A) with a fluoropolymer chain segment (Segment B) in the form of  
10 blocks or a graft; or by combining Segment C with Segment D in the form of blocks or a graft. As a result, the polymer according to the invention is remarkably improved in mechanical properties, high-temperature mechanical properties and heat resistance and other characteristics,  
15 as compared with the above-mentioned mere blend of polymers corresponding to Segments A and B. Further, when the polymer of the invention is used as a solid polyelectrolyte material in a fuel cell, it effectively improves the heat resistance, durability and creep  
20 resistance, thus increasing the reliability. Moreover, the polymer of the invention has higher ion conductivity than the blend of the segments, since the polymer has, in one molecule, Segment A (or Segment C) having ion conductivity and Segment B (or Segment D) capable of  
25 imparting mechanical properties, and consists of polymer

molecules having more homogeneous composition.

The first preferred embodiment of the multi-segmented fluoropolymer for use in the solid polyelectrolyte of the invention comprises:

- 5 (Segment A) a fluoropolymer chain segment containing sulfonic acid functional groups; and  
(Segment B): a polymer chain segment containing no sulfonic acid functional groups.

- 10 The second preferred embodiment of the multi-segmented fluoropolymer for use in the solid polyelectrolyte of the invention comprises:  
(Segment C) a fluoropolymer chain segment with a higher sulfonic acid functional group content; and  
(Segment D) a polymer chain segment with a lower sulfonic  
15 acid functional group content.

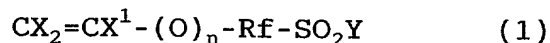
- Segment A in the multi-segmented fluoropolymer for use in the solid polyelectrolyte of the present invention contains sulfonic acid functional groups to impart ion conductivity necessary for a solid  
20 polyelectrolyte. Specifically stated, Segment A is a copolymer chain containing:  
(a) a fluoromonomer unit containing sulfonic acid functional groups; and  
(b) at least one type of ethylenic fluoromonomer unit  
25 copolymerizable with the monomer unit (a) and

containing no sulfonic acid functional groups.

Segments C and D in the multi-segmented fluoropolymer for use in the solid polyelectrolyte of the invention have sulfonic acid functional groups to impart ion conductivity necessary for a solid electrolyte. Specifically stated, Segments C and D are each a copolymer chain containing:

- (c) the above ethylenic fluoromonomer unit containing sulfonic acid functional groups; and
- (d) at least one ethylenic fluoromonomer unit copolymerizable with the unit (c) and containing no sulfonic acid functional groups.

Specifically stated, the sulfonic acid functional group-containing ethylenic fluoromonomer units (a) and (c), which form Segment A, C or D, are each a monomer represented by Formula (1)



wherein X and X<sup>1</sup> are the same or different, and are each hydrogen or fluorine; Y is F, Cl or OY<sup>1</sup> (Y<sup>1</sup> is hydrogen, alkali metal or C<sub>1</sub> to C<sub>5</sub> alkyl); Rf is C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene or C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene having ether bond(s); and n is 0 or 1. Particularly preferred is a monomer represented by Formula (2)



wherein Y and Rf are as defined for Formula (1). Specific

examples of the monomers of Formula (2) include:

- $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{SO}_3\text{H},$   
 $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{H},$   
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{SO}_3\text{H},$   
5  $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CH}_2\text{SO}_3\text{H},$   
 $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CF}_2\text{SO}_3\text{H},$   
 $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CH}_2\text{SO}_3\text{H},$   
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{SO}_2\text{F},$   
 $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F},$   
10  $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{F},$   
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CH}_2\text{SO}_2\text{F},$   
 $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{F},$   
 $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CH}_2\text{SO}_2\text{F},$   
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{SO}_3\text{Y}^2,$   
15  $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{Y}^2,$   
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{SO}_3\text{Y}^2,$   
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CH}_2\text{SO}_3\text{Y}^2,$   
 $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CF}_2\text{SO}_3\text{Y}^2,$  and  
 $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CH}_2-\text{SO}_3\text{Y}^2$   
20 (wherein  $\text{Y}^2$  is an alkali metal).

The monomer units (b) and (d) constituting Segment A, C or D may be each a monomer unit other than the monomer units (a) and (c), but are selected from ethylenic fluoromonomers containing substantially no functional groups. Specific examples include

tetrafluoroethylene (TFE), hexafluoropropylene (HFP),  
chlorotrifluoroethylene (CTFE), vinylidene fluoride (VdF),  
vinyl fluoride, perfluoro(alkylvinyl ethers) (PAVEs),  
hexafluoroisobutene,  $\text{CH}_2=\text{CF}-(\text{CF}_2)_n-\text{X}$  and  $\text{CH}_2=\text{CH}-(\text{CF}_2)_n-\text{X}$   
5 (wherein X is H, Cl or F; and n is an integer of 1 to 5).

In addition to the ethylenic fluoromonomer, a  
fluorine-free ethylenic monomer may be used in the  
copolymerization, within a range that does not lower the  
alkali resistance, heat resistance or heat durability.

10 The optional fluorine-free ethylenic monomer, when  
employed, is preferably an ethylenic monomer having 5 or  
less carbon atoms so as not to reduce the heat resistance.  
Specific examples of such ethylenic monomers include  
ethylene, propylene, 1-butene and 2-butene.

15 From the viewpoints of ion conductivity, acid  
resistance, alkali resistance, heat resistance and  
durability, it is preferable that Segments A, C and D are  
each a copolymer chain having a sulfonic acid functional  
group-containing monomer unit represented by Formula (2)  
20 and a perhaloolefin unit, in particular a copolymer chain  
having a sulfonic acid functional group-containing monomer  
unit represented by Formula (2) and a tetrafluoroolefin  
unit.

The sulfonic acid functional group content of  
25 Segment A, i.e., the amount of the sulfonic acid

functional group-containing fluoromonomer unit relative to the polymer chain segment A alone, is selected according to desired ion conductivity and mechanical properties of the polyelectrolyte, and is usually 5 mol% to 80 mol%,  
5 preferably 7 mol% to 70 mol%, more preferably 10 mol% to 50 mol%.

Segment B in the multi-segmented fluoropolymer comprising Segments A and B according to the invention is not limited as long as it is a polymer chain capable of  
10 imparting necessary mechanical properties to a solid polyelectrolyte, and can be selected according to the kind of Segment A and the purposes. As described before, it is preferable that Segment B is a crystalline polymer chain, or an amorphous polymer chain having a high glass  
15 transition point of 100°C or higher, in particular 200°C or higher.

Among monomers which can form Segment B, usable fluoropolymers include, for example, at least one of TFE, CTFE, PAVE, HFP,  $\text{CF}_2=\text{CF}-(\text{CF}_2)_p-\text{X}$  (wherein p is an integer  
20 of 1 to 10, and X is F or Cl), perfluoro-2-butene and like perhaloolefins, VdF, vinyl fluoride, trifluoroethylene,  $\text{CH}_2=\text{CX}^1-(\text{CF}_2)_q-\text{X}^2$  (wherein  $\text{X}^1$  and  $\text{X}^2$  are each H or F, and q is an integer of 1 to 10),  $\text{CH}_2=\text{C}(\text{CF}_3)_2$  and like partially fluorinated olefins. Also, at least one monomer  
25 copolymerizable with the above monomers, such as ethylene,

propylene, vinyl chloride, vinyl ethers, vinyl carboxylate esters or acrylic monomers, can be used as a copolymerization component.

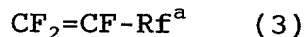
From the viewpoints of acid resistance, alkali resistance, heat resistance and durability, preferably usable as the main component is a fluoroolefin by itself, a combination of fluoroolefins, a combination of ethylene with TFE, and a combination of ethylene with CTFE. Particularly preferred is a combination of perhaloolefins.

Specific examples of usable main components are:

- (1) VdF/TFE (0~100/100~0), in particular VdF/TFE (70~99/30~1), PTFE or PVdF;
- (2) ethylene/TFE/HFP (6~43/40~81/10~30), 3,3,3-trifluoropropylene-1,2-trifluoromethyl-3,3,3-trifluoropropylene-1/PAVE (40~60/60~40);
- (3) TFE/CF<sub>2</sub>=CF-Rf (wherein Rf is as defined above, the percentage of CF<sub>2</sub>=CF-Rf being less than 15 mol%);
- (4) VdF/TFE/CTFE (50~99/30~0/20~1);
- (5) VdF/TFE/CTFE (50~99/30~0/20~1);
- (6) ethylene/TFE (30~60/70~40);
- (7) polychlorotrifluoroethylene (PCTFE); and
- (8) ethylene/CTFE (30~60/70~40).

Among the above examples, particularly preferred is a polymer chain comprising 85 mol% to 100 mol% of tetrafluoroethylene and 15 mol% to 0 mol% of a monomer

represented by Formula



wherein  $\text{Rf}^{\text{a}}$  is  $\text{CF}_3$  or  $\text{ORf}^{\text{b}}$  (wherein  $\text{Rf}^{\text{b}}$  is  $\text{C}_1$  to  $\text{C}_5$  perfluoroalkyl). When the polymer chain is combined with  
5 the above-mentioned Segment A to form a segmented polymer, a material can be obtained which is suitable for a solid polyelectrolyte and has all of ion conductivity, acid resistance, alkali resistance, heat resistance, durability and good mechanical properties.

10 In the multi-segmented fluoropolymer comprising Segments C and D, the sulfonic acid functional group content of Segment C, i.e., the amount of sulfonic acid functional group-containing fluoromonomer unit relative to the polymer chain segment C alone, can be selected  
15 according to desired ion conductivity and mechanical properties of the solid polyelectrolyte, and is usually about 10 mol% to 60 mol%, preferably 13 mol% to 50 mol%, more preferably 20 mol% to 40 mol%.

The sulfonic acid functional group content of  
20 Segment D, i.e., the amount of sulfonic acid functional group-containing fluoropolymer unit in the polymer chain segment D alone, can be selected according to desired ion conductivity and mechanical properties of the solid polyelectrolyte, and is usually 0.1 mol% to 20 mol%,  
25 preferably 1 mol% to 13 mol%, more preferably 1 mol% to 10



The sulfonic acid functional group content of the segmented fluoropolymer comprising Segments A and B is 10 mol% to 60 mol%, preferably 13 mol% to 50 mol%, more preferably 20 mol% to 40 mol%.

The process for combining Segment A with Segment B, or Segment C with Segment D, to form a segmented polymer can be selected according to whether the segmented polymer is a graft polymer or a block polymer. The iodine transfer polymerization can be employed to effectively synthesize a block segmented polymer of a structure such as: A-B, B-A-B or A-B-A; or C-D, D-C-D or C-D-C, with a high percentage of block formation.

(Segment A or C)

For Example, monomers (a) and (b) for forming  
25 Segment A are subjected to emulsion polymerization under

substantially anoxic conditions in an aqueous medium in the presence of an iodine compound, preferably a diiodine compound, under pressure with stirring, using a radical polymerization initiator.

5               Segment C can be synthesized in the same manner as above except using the monomers (c) and (d) for forming Segment C in place of the monomers (a) and (b).

Typical examples of usable diiodine compounds include 1,3-diiodide perfluoropropane, 1,4-diiodide  
10 perfluorobutane, 1,3-diiodide-2-chloroperfluoropropane, 1,5-diiodide-2,4-dichloroperfluoropentane, 1,6-diiodide perfluorohexane, 1,8-diiodide perfluorooctane, 1,12-diiodide perfluorododecane and 1,16-diiodide perfluorohexadecane, diiodide methane and 1,2-diiodide  
15 ethane. These compounds may be used singly or in combination. Among these compounds, 1,4-diiodide perfluorobutane is preferable. The amount of the diiodine compound is 1.01 to 1 wt.% based on the total weight of Segment A or C.

20               In the present invention, the radical polymerization initiator for use in the preparation of Segment A or C may be any of radical polymerization initiators conventionally used for preparation of a fluoroelastomer. Such initiators include organic or  
25 inorganic peroxides and azo compounds. Typical initiators

003727 58700/60

include persulfuric acid salts, carbonate peroxides and ester peroxides, and preferred initiators include ammonium persulfate (APS). APS may be used singly, or may be in combination with sulfites, sulfurous acid salts or like  
5 reducing agents.

The emulsifier for use in the emulsification polymerization can be selected from a wide range, and is preferably a salt of carboxylic acid having a fluorocarbon chain or a fluoropolyether chain, to inhibit chain  
10 transfer reaction to a molecule of the emulsifier during polymerization. The amount of the emulsifier to be used is preferably about 0.05 to 15 wt.%, in particular 0.2 to 10 wt.%, relative to water added.

The polymer for Segment A or C thus obtained has,  
15 at its end portions (for example, at both ends), an iodine atom which serves as a starting point for polymerization to form the polymer chain segment B or D.

(Block polymerization to form Segment B or D)

Block polymerization to form Segment B or D can  
20 be carried out subsequent to the emulsification polymerization to obtain Segment A or C, using the monomers for forming Segment B or D, to thereby obtain a block segmented polymer having a structure of B-A-B or D-C-D.

25 Preferred molecular weights of the segments of

the obtained segmented polymer are as follows.

Segment A: 5000 to 1000000, in particular 20000 to 500000;

Segment B (total molecular weight of Segment B's at both ends): 1000 to 1200000, in particular 3000 to 600000;

5 Segment C: 1000 to 1000000, in particular 10000 to 500000;

Segment D (total molecular weight of Segment D's at both ends): 1000 to 1200000, in particular 3000 to 600000.

Too low a molecular weight results in insufficient mechanical properties, whereas too high a molecular weight  
10 impairs properties for forming a film or membrane.

The ratio of Segment A to Segment B (total of Segment B's at both ends) in the segmented polymer of the invention comprising Segments A and B is selected according to desired ion conductivity, mechanical  
15 properties and other characteristics of the solid polyelectrolyte. The ratio is selected preferably from the range of Segment A : Segment B = 5:95 to 98:2 (wt.%), more preferably from the range of Segment A : Segment B = 20:80 to 95:5 (wt.%), particularly from the range of  
20 Segment A : Segment B = 30:70 to 90:10 (wt.%).

Too small a proportion of Segment B fails to sufficiently improve the mechanical properties, whereas too large a proportion of Segment B results in insufficient ion conductivity.

25 The ratio of Segment C to Segment D (total of

Segment D's at both ends) in the segmented polymer of the invention comprising Segments C and D is selected according to desired ion conductivity, mechanical properties and like characteristics of the solid polyelectrolyte, and the composition of each segment. The ratio may be selected preferably from the range of Segment C : Segment D = 5:95 to 98:2 (wt.%), more preferably from the range of Segment C : Segment D = 20:80 to 95:5 (wt.%), particularly from the range of Segment C : Segment D = 30:70 to 90:10.

Too small a ratio of Segment B or D fails to sufficiently improve the mechanical properties, whereas too large a ratio of Segment B or D results in insufficient ion conductivity.

As stated above, a variety of segmented fluoropolymers containing sulfonic acid functional groups can be obtained. Among them, one having an equivalent weight of 400 to 1600 (based on the whole segmented polymer), as measured by a known neutralization titration method, is selected for use as a solid polyelectrolyte in fuel cells or the like. Particularly useful is one having an equivalent weight of 500 to 1200, preferably 700 to 1100, based on the whole segmented polymer.

In particular, to impart good mechanical properties to the whole segmented fluoropolymer comprising

segments C and D, it is suitable that the fluoropolymer chain segment D has an equivalent weight of at least 1000, preferably at least 1300, more preferably at least 1500.

Too large an equivalent weight results in  
5 insufficient ion conductivity, whereas too small an  
equivalent weight leads to excessive hydration, excessive  
swelling and excessive gas permeability of the segmented  
polymer, and also to lower mechanical properties.

As used herein, Segment A<sup>1</sup>, Segment B<sup>1</sup>, Segment  
10 C<sup>1</sup> and Segment D<sup>1</sup> are all included in the scopes of  
Segment A, Segment B, Segment C and Segment D,  
respectively.

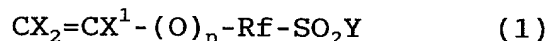
A multi-segmented fluoropolymer comprising a fluoropolymer chain segment A<sup>1</sup> and a fluoropolymer chain segment B<sup>1</sup> is a novel substance which is included in the scope of the multi-segmented fluoropolymer comprising the fluoropolymer chain segment A and the fluoropolymer chain segment B.

In the multi-segmented fluoropolymer comprising  
20 the fluoropolymer chain segment A<sup>1</sup> containing sulfonic  
acid functional groups and the fluoropolymer chain segment  
B<sup>1</sup> containing no sulfonic acid functional groups:

Segment A<sup>1</sup> is a copolymer having a molecular weight of 5000 to 750000 and comprising:

25 (e) 1 to 50 mol% of at least one type of structural unit

represented by Formula (1)

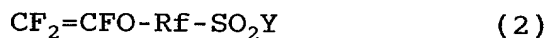


wherein X, X<sup>1</sup>, Y, n and Rf are as defined above, and

(f) 99 to 50 mol% of at least one type of ethylenic  
5 monomer structural unit containing no sulfonic acid  
functional groups; and

Segment B<sup>1</sup> is a fluoropolymer chain containing  
at least one type of ethylenic fluoromonomer unit and  
having a molecular weight of 3000 to 1200000.

10 The ethylenic fluoropolymer (e) containing  
sulfonic acid functional groups is preferably a compound  
represented by Formula (2)



wherein Y and Rf are as defined for Formula (1).

15 The ethylenic monomer (f) containing no sulfonic  
acid functional groups is preferably one selected from  
ethylenic fluoromonomers, more preferably  
tetrafluoroethylene.

Segment B<sup>1</sup> is preferably a polymer chain  
20 comprising 85 to 100 mol% of tetrafluoroethylene and 15 to  
0 mol% of a monomer represented by Formula (3)



wherein Rf<sup>a</sup> is CF<sub>3</sub> or ORf<sup>b</sup> (wherein Rf<sup>b</sup> is C<sub>1</sub> to C<sub>5</sub>  
perfluoroalkyl).

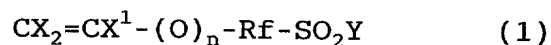
25 In the multi-segmented fluoropolymer comprising

003121 5310060

at least two types of fluoropolymer chain segments C<sup>1</sup> and D<sup>1</sup> containing sulfonic acid functional groups,

Segment C<sup>1</sup> is a copolymer having a molecular weight of 5000 to 750000 and comprising:

- 5 (g) 13 to 50 mol% of at least one type of ethylenic fluoromonomer structural unit containing sulfonic acid functional groups and represented by Formula (1)

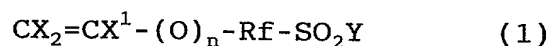


wherein X, X<sup>1</sup>, Y, n and Rf are as defined above, and

- 10 (h) 87 to 50 mol% of at least one type of ethylenic monomer structural unit containing no sulfonic acid functional groups; and

Segment D<sup>1</sup> is a fluoropolymer chain having a molecular weight of 3000 to 1200000 and comprising:

- 15 (i) not less than 0.1 mol% but less than 13 mol% of at least one type of ethylenic fluoromonomer structural unit containing sulfonic acid functional groups and represented by Formula (1)

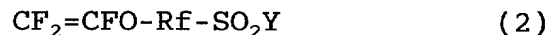


- 20 wherein X, X<sup>1</sup>, Y, n and Rf are as defined above; and  
(j) more than 87 mol% but not more than 99.9 mol% of at least one type of ethylenic monomer structural unit containing no sulfonic acid functional groups.

The ethylenic fluoromonomer (g) containing  
25 sulfonic acid functional groups is preferably a compound



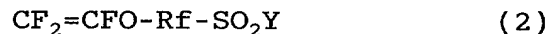
represented by Formula (2)



wherein Y and Rf are as defined for Formula (1).

The ethylenic monomer (h) containing no sulfonic  
5 acid functional groups is preferably one having at least  
one ethylenic fluoromonomer, more preferably  
tetrafluoroethylene.

The ethylenic fluoromonomer (i) containing  
sulfonic acid functional groups is preferably a compound  
10 represented by Formula (2)



wherein Y and Rf are as defined for Formula (2).

The ethylenic monomer (j) containing no sulfonic  
acid functional groups is preferably one having at least  
15 one ethylenic fluoromonomer, more preferably  
tetrafluoroethylene.

A solid polyelectrolyte membrane can be prepared  
by a conventional process using the multi-segmented  
fluoropolymer of the present invention.

20 In the solid polyelectrolyte membrane, the  
multi-segmented fluoropolymer preferably contains  
protonated sulfonic acid ( $\text{SO}_3\text{H}$ ) groups as the sulfonic  
acid functional groups. The solid polyelectrolyte  
membrane preferably has a modulus of elasticity of at  
25 least  $1 \times 10^8$  dyn/cm<sup>2</sup> at 110°C or higher, more preferably at

least  $1 \times 10^8$  dyn/cm<sup>2</sup> at 150°C or higher, most preferably at least  $3 \times 10^8$  dyn/cm<sup>2</sup> at 110°C or higher.

The solid polyelectrolyte membrane of the present invention has an equivalent weight, based on the whole multi-segmented fluoropolymer, of 1600 or less, preferably 1100 or less, more preferably 1000 or less, still more preferably 900 or less, particularly 800 or less.

The solid polyelectrolyte membrane has a thickness of about 30  $\mu$ m to 500  $\mu$ m, preferably 40  $\mu$ m to 400  $\mu$ m, more preferably 50  $\mu$ m to 300  $\mu$ m, on a dry weight basis.

The solid polyelectrolyte material or solid polyelectrolyte membrane of the invention can be utilized to prepare a fuel cell.

Fuel cell components other than the solid polyelectrolyte material or solid polyelectrolyte membrane are not limited, and may be any of those known. For example, usable as a gas diffusion electrode is a porous sheet to which a conductive carbon black powder bearing a particulate platinum catalyst is bonded with PTFE, FEP or like hydrophobic resin binder.

#### BEST MODE FOR CARRYING OUT THE INVENTION

The following examples and comparative examples are provided to illustrate the present invention in

further detail, and not to limit the scope of the invention.

Synthesis Example 1 (Synthesis of fluoropolymer chain containing sulfonic acid fluoride groups, corresponding to  
5 Segment A or C)

A 500 ml stainless steel autoclave equipped with a stirrer, a thermometer and a pressure gauge was charged with 225 g of pure water, 25 g of an emulsifier represented by Formula (4)

10 
$$\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{COONH}_4 \quad (4),$$

5.0 g of a monomer containing sulfonic acid fluoride groups (hereinafter referred to briefly as "PFSF") represented by Formula (5)

$$\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F} \quad (5),$$

15 and 0.1 g of a diiodine compound I-(CF<sub>2</sub>)<sub>4</sub>-I. After fully purging the system with nitrogen gas, the internal temperature was maintained at 60°C with stirring, and tetrafluoroethylene gas was supplied so that the internal pressure became 1.5 kgf/cm<sup>2</sup>G. Then, 5.0 ml of 0.1%  
20 aqueous solution of ammonium persulfate (APS) was injected under nitrogen pressure to initiate a reaction. The pressure decreased as the polymerization reaction proceeded, and when the pressure decreased to 1.0 kgf/cm<sup>2</sup>G, tetrafluoroethylene gas was supplied to increase the  
25 pressure to 1.5 kgf/cm<sup>2</sup>G. The decrease and increase of

the pressure were repeated. From the start of the polymerization, while continually supplying tetrafluoroethylene gas, 2.5 g of the sulfonic acid fluoride group-containing monomer (PFSF) was injected each  
5 time 1.5 g of tetrafluoroethylene gas was consumed, to continue polymerization. Tetrafluoroethylene gas was supplied 9 times (22.5 g) in total. When 15 g of tetrafluoroethylene gas was consumed, the supply was stopped. Then, the autoclave was cooled, and unreacted  
10 monomers were released, giving 293 g of an aqueous dispersion having a solid concentration of 13.6%.

1 g of the aqueous dispersion was taken, and frozen for coagulation. After thawing, the coagulation product was washed with water and vacuum-dried to obtain a  
15 white polymer.

The obtained white polymer was completely soluble in perfluorobenzene, HCFC-225 or like fluorine-containing solvent.

<sup>19</sup>F-NMR analysis revealed that the monomer  
20 composition of the polymer was TFE/PFSF=74.5/25.5 mol%.

No crystalline melting point was observed in DSC analysis.

Example 1 [Block copolymerization to form Segment B (B-A-B)]

25 The same 500 ml autoclave as used in Synthesis

Example 1 was charged with 120 g of the aqueous dispersion of the sulfonic acid fluoride group-containing fluoropolymer obtained in Synthesis Example 1 (having a concentration of 13.6%) and 120 g of pure water. After  
5 fully purging the system with nitrogen gas, the internal temperature was maintained at 60°C with stirring.

A gaseous monomer mixture of tetrafluoroethylene/perfluoropropylvinyl ether (PPVE) (97 mol%/3 mol%) previously prepared in a cylinder, was  
10 injected so that the internal pressure became 7.5 kgf/cm<sup>2</sup>G. Then, 3 ml of 0.1% aqueous solution of ammonium persulfate (APS) was injected under nitrogen pressure to initiate a reaction. The pressure decreased as the polymerization reaction proceeded, and when the pressure decreased to 7.0  
15 kgf/cm<sup>2</sup>G, the above gaseous monomer mixture was supplied to increase the pressure to 7.5 kgf/cm<sup>2</sup>G. The decrease and increase of the pressure were repeated, while supplying the tetrafluoroethylene/PPVE gaseous monomer mixture. When 7.0 g of the gaseous monomer mixture was  
20 consumed from the start of the polymerization, the supply was stopped. Then, the autoclave was cooled and unreacted monomers were released, giving 245 g of an aqueous dispersion having a solid concentration of 9.5%. The percentage of Segment B to the whole polymer was  
25 calculated from the increase in amount of the polymer:

$$\frac{\{(\text{Amount of polymer obtained by second polymerization}) - (\text{Amount of polymer used in second polymerization})\}}{(\text{Amount of polymer obtained by second polymerization})} \times 100 = 30\%$$

The aqueous dispersion was frozen for  
5 coagulation, and the coagulated polymer was washed with  
water and dried to obtain a white polymer.

The obtained polymer was insoluble in perfluorobenzene, HCFC-225 or like fluorine-containing solvents.

10 <sup>19</sup>F-NMR analysis revealed that the monomer composition of the whole segmented polymer was TFE/PFSF/PPVE=85.1 mol%/13.9 mol%/1.0 mol%.

DSC analysis observed a crystalline melting point at 303°C, which was attributable to Segment B added by the second polymerization.

Example 2 [Block copolymerization to form Segment B (B-A-B)]

The procedure of Example 1 was followed. That is, the 500 ml autoclave was charged with 120 g of the aqueous dispersion obtained in Synthesis Example 1 (concentration: 13.6%) and 120 g of water. After fully purging the system with nitrogen gas, the internal temperature was maintained at 60°C with stirring.

A gaseous monomer mixture of

25 tetrafluoroethylene/perfluoro(propylvinyl ether) (97

mol%/3 mol%) previously prepared in a cylinder was injected so that the internal pressure became 6.0 kgf/cm<sup>2</sup>G. Subsequently, 1.5 ml of a 0.1% aqueous solution of ammonium persulfate (APS) was injected under nitrogen pressure to initiate a reaction. The pressure decreased as the polymerization reaction proceeded, and when the pressure decreased to 5.5kgf/cm<sup>2</sup>G, the above gaseous monomer mixture was supplied to increase the pressure to 6.0 kgf/cm<sup>2</sup>G. The decrease and increase of the pressure were repeated while supplying the tetrafluoroethylene/PPFE gaseous monomer mixture. When 3.3 g of the gaseous monomer mixture was consumed from the start of the polymerization, the supply was stopped. Then, the autoclave was cooled, and the unreacted monomers were released, giving 249 g of an aqueous dispersion having a solid concentration of 7.9%. The percentage of Segment B to the whole polymer was calculated from the increase in amount of the polymer:

$$\frac{\{(\text{Amount of polymer obtained by second polymerization}) - (\text{Amount of polymer used in second polymerization})\}}{(\text{Amount of polymer obtained by second polymerization})} \times 100 = 17\%$$

The aqueous dispersion was frozen for coagulation, and the coagulated polymer was washed with water and dried to obtain a white polymer.

The obtained polymer was insoluble in

perfluorobenzene, HCFC-225 or like fluorine-containing solvent.

<sup>19</sup>F-NMR analysis revealed that the monomer composition of the whole segmented polymer was

5 TFE/PFSF/PPVE=81.8 mol%/17.7 mol%/0.5 mol%.

DSC analysis observed a crystalline melting point at 301°C, which was attributable to Segment B added by the second polymerization.

Example 3 (Measurement of equivalent weight, water content  
10 and dynamic viscoelasticity)

The segmented fluoropolymer containing sulfonic acid fluoride (-SO<sub>2</sub>F) groups and obtained in Example 1 was used. The sulfonic acid fluoride groups were hydrolyzed in the manner described above, for conversion into  
15 sulfonic acid (-SO<sub>3</sub>H) groups. Thereafter, the equivalent weight, water content and dynamic viscoelasticity were measured. Table 1 shows the results.

(1) Hydrolysis of -SO<sub>2</sub>F groups

The white solid obtained in Example 1 was fully  
20 impregnated with an aqueous solution of 25% NaOH, and allowed to stand at 90°C for 8 hours. The solid was then impregnated with an aqueous solution of 6N HCl at room temperature for 4 hours, followed by drying at 110°C for 6 hours.

25 (2) Measurement of equivalent weight



Equivalent weight means weight (g) of a polymer necessary to completely neutralize 1 equivalent of a base (for example, 1 equivalent of sodium hydroxide). Using a predetermined amount of the segmented fluoropolymer after hydrolysis and drying, the  $\text{SO}_3\text{H}$  groups in the polymer were completely neutralized in an aqueous solution of excess NaOH. The amount of NaOH remaining after the neutralization was determined by titration with an aqueous solution of 0.1N HCL to calculate the equivalent weight of NaOH that had participated in the neutralization (reverse titration). Then, the equivalent weight of the polymer was calculated.

Further, a film was prepared in the following manner using the polymer of Example 1. The water content and dynamic viscoelasticity of the obtained water-containing film were measured.

### (3) Film preparation

The segmented fluoropolymer containing  $-\text{SO}_2\text{F}$  groups and obtained in Example 1 was placed in a mold of 100 mm diameter, and the mold was mounted on a pressing machine set at  $350^\circ\text{C}$ . After 20-minute preliminary heating, compression molding was performed at  $70 \text{ kg/cm}^2$  for 1 minute to obtain a 0.2 mm thick film. The obtained film containing  $-\text{SO}_2\text{F}$  groups was treated in the same manner as in (1) for hydrolysis and drying.

After wiping off water drops from the film surface and

The water content was calculated according to the following equation:

(5) Calculation of modulus in tension from measurement of dynamic viscoelasticity

15 Immediately after incorporation of water, a rectangle  
(about 35 mm  $\times$  5 mm) was cut out from the film and set on  
a viscoelasticity measuring device RSA-2 (a product of  
Rheometric) to measure the modulus in tension at a  
frequency of 1 Hz at various temperatures. Table 1 and  
20 Fig. 2 show the results.

Hydrolysis, measurement of the equivalent weight, film preparation and measurement of water content were performed in the same manner as in Example 3 except using

the segmented fluoropolymer containing sulfonic acid fluoride ( $-\text{SO}_2\text{F}$ ) groups obtained in Example 2. Table 1 shows the results.

#### Comparative Example 1

5           The equivalent weight, water content and dynamic viscoelasticity of a Nafion® 117 membrane (manufactured by Du pont, a film having a thickness of 7 mil, i.e., about 170  $\mu\text{m}$ , in a dry state) were measured in the same manner as in Example 3. Table 1 and Fig. 2 show the results.

10

Table 1

	Ex. 3	Ex. 4	Ex. 5
Test sample	Ex. 1	Ex. 2	Nafion 117
M.p.(°C) of Segment B	303	301	-
Percentage of Segment B (wt.%)	30	17	-
Equivalent weight	1090	990	-
Water content (%)	28	30	32
Modulus in tension ( $\text{dyn}/\text{cm}^2$ )			
25°C	$1.7 \times 10^9$	-	$2.7 \times 10^9$
50°C	$2.4 \times 10^9$	-	$2.5 \times 10^9$
110°C	$1.0 \times 10^9$	-	$1.6 \times 10^8$
150°C	$3.9 \times 10^8$	-	Melted
200°C	$2.1 \times 10^8$	-	Melted

Example 5 [Block copolymerization to form Segment D (D-C-D)]

In the same manner as in Example 1, the 500 ml

autoclave was charged with 120 g of the aqueous dispersion (concentration: 13.6%) obtained in Synthesis Example 1 and 120 g of pure water. After fully purging the system with nitrogen gas, the internal temperature was maintained at  
5 60°C with stirring.

Tetrafluoroethylene gas was injected so that the internal pressure became 1.5 kgf/cm<sup>2</sup>G. Then, 1.5 ml of an aqueous solution of 0.1% ammonium persulfate (APS) was injected under nitrogen pressure to initiate a reaction.  
10 The pressure decreased as the polymerization reaction proceeded, and when the pressure decreased to 1.0 kgf/cm<sup>2</sup>G, the above gaseous monomer mixture was supplied to increase the pressure to 1.5 kgf/cm<sup>2</sup>G. The decrease and increase of the pressure were repeated. From the start of the  
15 polymerization, while continually supplying tetrafluoroethylene gas, 0.5 g of the monomer containing sulfonic acid fluoride groups (PFSF) was injected each time 1.2 g of tetrafluoroethylene gas was consumed, to thereby continue the polymerization. The monomer  
20 containing sulfonic acid fluoride groups was supplied 9 times (4.5 g) in total. When 12 g of tetrafluoroethylene gas was consumed, the supply was stopped. Then, the autoclave was cooled, and unreacted monomers were released, giving 257 g of an aqueous dispersion having a solid  
25 concentration of 13.0%.

The percentage of Segment D to the whole polymer was calculated from the increase in amount of the polymer: 
$$\frac{\{(\text{Amount of the polymer obtained by the second polymerization}) - (\text{Amount of the polymer used in the second polymerization})\}}{(\text{Amount of the polymer obtained by the second polymerization})} = 51.1\%$$

In the same manner as in Example 1, the obtained aqueous dispersion was frozen for coagulation, and the coagulation product was washed with water and dried, to thereby isolate a white solid.

The obtained white solid was insoluble in fluorine-containing solvents such as perfluorobenzene and HCFC-225.

<sup>19</sup>F-NMR analysis revealed that the monomer composition of the whole segmented polymer was TFE/PFSF=85 mol%/15 mol%.

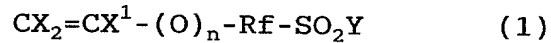
The monomer composition of Segment D calculated from the compositions of the whole polymer and the polymer obtained in Synthesis Example 1 was TFE/PFSF=92 mol%/8 mol%.

DSC analysis observed a crystalline melting point at 285°C, which was attributable to Segment D added by the second polymerization.

The hydrolysate of the dry polymer had an equivalent weight of 1040.



acid functional groups is represented by Formula (1)

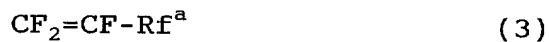


wherein X and X<sup>1</sup> may be the same or different and are each hydrogen or fluorine; Y is F, Cl or OY<sup>1</sup> wherein Y<sup>1</sup> is

5 hydrogen, alkali metal or C<sub>1</sub> to C<sub>5</sub> alkyl; R<sub>f</sub> is C<sub>1</sub> to C<sub>40</sub>  
divalent fluoroalkylene or C<sub>1</sub> to C<sub>40</sub> divalent  
fluoroalkylene having ether bond(s); and n is 0 or 1.

5. The material according to Claim 3, wherein  
the at least one type of ethylenic fluoromonomer unit (b)  
10 containing no sulfonic acid functional groups is  
tetrafluoroethylene.

6. The material according to Claim 2, wherein the fluoropolymer chain segment B is a polymer chain comprising 85 to 100 mol% of tetrafluoroethylene and 15 to 15 0 mol% of a monomer represented by Formula (3)



wherein  $Rf^a$  is  $CF_3$  or  $ORf^b$  wherein  $Rf^b$  is  $C_1$  to  $C_5$  perfluoroalkyl.

7. The material according to Claim 2, wherein  
20 the multi-segmented fluoropolymer has an equivalent weight  
of 400 to 1600.

8. The material according to Claim 1, which comprises a multi-segmented fluoropolymer having at least two types of fluoropolymer chain segments C and D containing sulfonic acid functional groups, the

fluoropolymer chain segment C having a smaller equivalent weight than the fluoropolymer chain segment D.

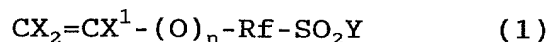
9. The material according to Claim 8, wherein  
the fluoropolymer chain segment D has a crystalline  
melting point of 100°C or higher or a glass transition  
5 melting point of 100°C or higher.

10. The material according to Claim 8, wherein the fluoropolymer chain segments C and D containing sulfonic acid functional groups are each a copolymer comprising:

(c) an ethylenic fluoromonomer unit containing sulfonic acid functional groups; and

(d) at least one type of ethylenic fluoromonomer unit copolymerizable with the unit (c) and containing no sulfonic acid functional groups.

11. The material according to Claim 10, wherein the ethylenic fluoromonomer unit (c) containing sulfonic acid functional groups is represented by Formula (1)



20 wherein X, X<sup>1</sup>, Y, n and Rf are as defined above.

12. The material according to Claim 8, which is the multi-segmented fluoropolymer in which the fluoropolymer chain segment D has an equivalent weight of 1000 or more.

25           13. A material according to Claim 8, wherein the



multi-segmented fluoropolymer has an equivalent weight of 400 to 1600.

14. A solid polyelectrolyte membrane comprising the multi-segmented fluoropolymer according to Claim 2 or 8.

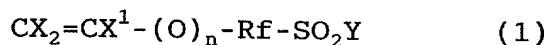
15. The solid polyelectrolyte membrane according to Claim 14, wherein the multi-segmented fluoropolymer contains protonated sulfonic acid ( $\text{SO}_3\text{H}$ ) groups as the sulfonic acid functional groups, and has a modulus of elasticity of at least  $1 \times 10^8$  dyn/cm<sup>2</sup> at 110°C or higher.

16. The solid polyelectrolyte membrane according to Claim 15, wherein the equivalent weight of the whole multi-segmented fluoropolymer is 1600 or less.

17. A multi-segmented fluoropolymer having a fluoropolymer chain segment  $\text{A}^1$  containing sulfonic acid functional groups and a fluoropolymer chain segment  $\text{B}^1$  containing no sulfonic acid functional groups, wherein:

the fluoropolymer chain segment  $\text{A}^1$  containing sulfonic acid functional groups is a copolymer having a molecular weight of 5000 to 750000 and comprising:

(e) 1 to 50 mole% of at least one type of structural unit represented by Formula (1)



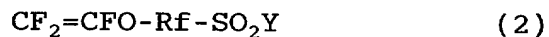
wherein X,  $\text{X}^1$ , Y, n and Rf are as defined above, and

(f) 99 to 50 mol% of at least one type of ethylenic

monomer structural unit containing no sulfonic acid functional groups; and

the fluoropolymer chain segment B<sup>1</sup> is a fluoropolymer chain containing at least one type of ethylenic fluoromonomer unit and having a molecular weight of 3000 to 1200000.

18. The multi-segmented fluoropolymer according to Claim 17, wherein the ethylenic fluoromonomer (e) in the fluoropolymer chain segment A<sup>1</sup> is represented by Formula (2)

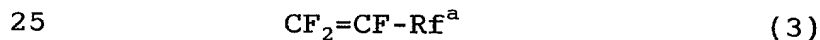


wherein Y and Rf are as defined for Formula (1).

19. The multi-segmented fluoropolymer according to Claim 17, wherein the ethylenic monomer (f) in the fluoropolymer chain segment A<sup>1</sup> contains at least one ethylenic fluoromonomer.

20. The multi-segmented fluoropolymer according to Claim 19, wherein the ethylenic monomer (f) is tetrafluoroethylene.

21. The multi-segmented fluoropolymer according to Claim 17, wherein the fluoropolymer chain segment B<sup>1</sup> is a polymer chain comprising 85 to 10 mol% of tetrafluoroethylene and 15 to 0 mol% of a monomer represented by Formula (3)

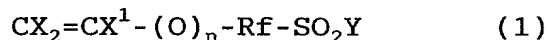


wherein  $Rf^a$  is  $CF_3$  or  $ORf^b$  wherein  $Rf^b$  is  $C_1$  to  $C_5$  perfluoroalkyl.

22. A multi-segmented fluoropolymer having at least two types of fluoropolymer chain segments  $C^1$  and  $D^1$  containing sulfonic acid functional groups, wherein:

the fluoropolymer chain segment  $C^1$  is a copolymer having a molecular weight of 5000 to 750000 and comprising:

(g) 13 to 50 mol% of at least one type of ethylenic fluoromonomer structural unit containing sulfonic acid functional groups and represented by Formula (1)

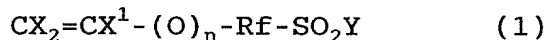


wherein  $X$ ,  $X^1$ ,  $Y$ ,  $n$  and  $Rf$  are as defined above, and

(h) 87 to 50 mol% of at least one type of ethylenic monomer structural unit containing no sulfonic acid functional groups; and

the fluoropolymer chain segment  $D^1$  is a fluoropolymer chain having a molecular weight of 3000 to 1200000 and comprising:

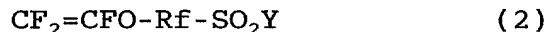
(i) not less than 0.1 mol% but less than 13 mol% of at least one type of ethylenic fluoromonomer unit containing sulfonic acid functional groups and represented by Formula (1)



wherein  $X$ ,  $X^1$ ,  $Y$ ,  $n$  and  $Rf$  are as defined above, and

(j) more than 87 mol% but not more than 99.9 mol% of at least one type of ethylenic monomer unit containing no sulfonic acid functional groups.

23. The multi-segmented fluoropolymer according to Claim 22, wherein the ethylenic fluoromonomer (g) in the fluoropolymer chain segment C<sup>1</sup> is represented by Formula (2)

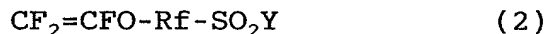


wherein Y and Rf are as defined for Formula (1).

24. The multi-segmented fluoropolymer according to Claim 22, wherein the ethylenic monomer (h) in the fluoropolymer chain segment C<sup>1</sup> contains at least one ethylenic fluoromonomer.

25. The multi-segmented fluoropolymer according to Claim 24, wherein the ethylenic monomer (h) in the fluoropolymer chain segment C<sup>1</sup> is tetrafluoroethylene.

26. The multi-segmented fluoropolymer according to Claim 22, wherein the ethylenic fluoromonomer (i) in the fluoropolymer chain segment D<sup>1</sup> is represented by Formula (2)



wherein Y and Rf are as defined for Formula (1).

27. The multi-segmented fluoropolymer according to Claim 22, wherein the ethylenic monomer (j) in the fluoropolymer chain segment D<sup>1</sup> contains at least one

28. The multi-segmented fluoropolymer according to Claim 27, wherein the ethylenic monomer (j) in the fluoropolymer chain segment D<sup>1</sup> is tetrafluoroethylene.

1 / 1

Fig. 1

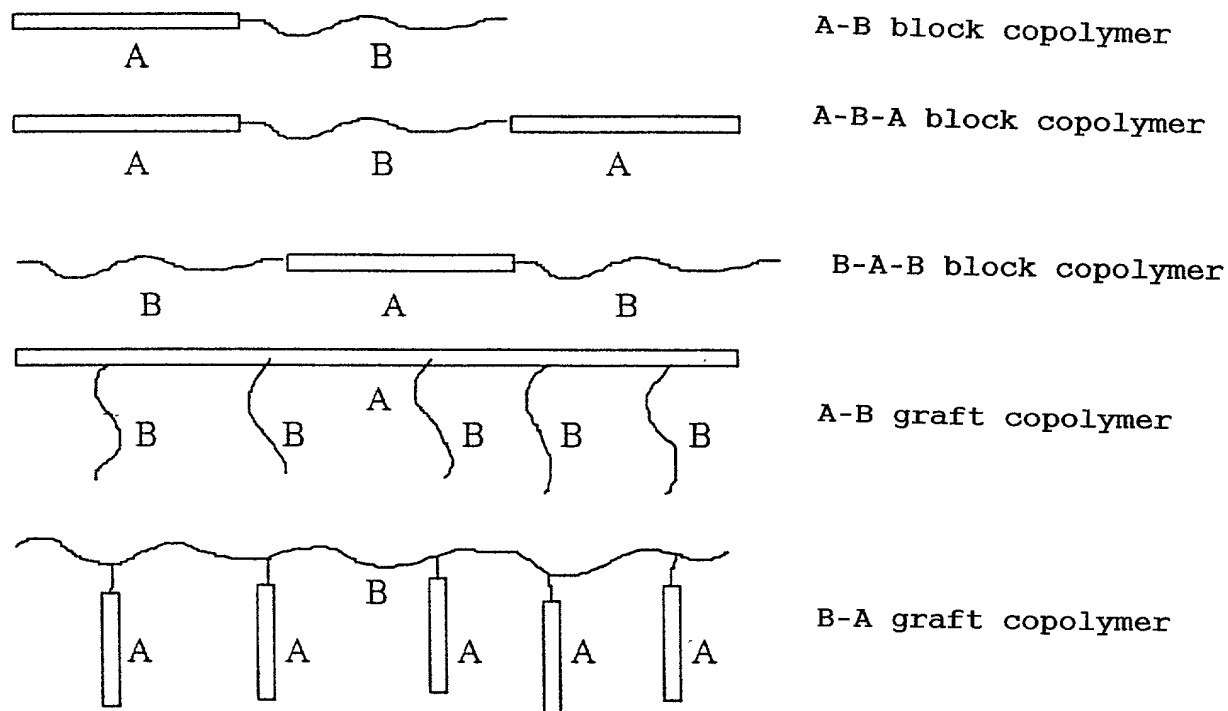
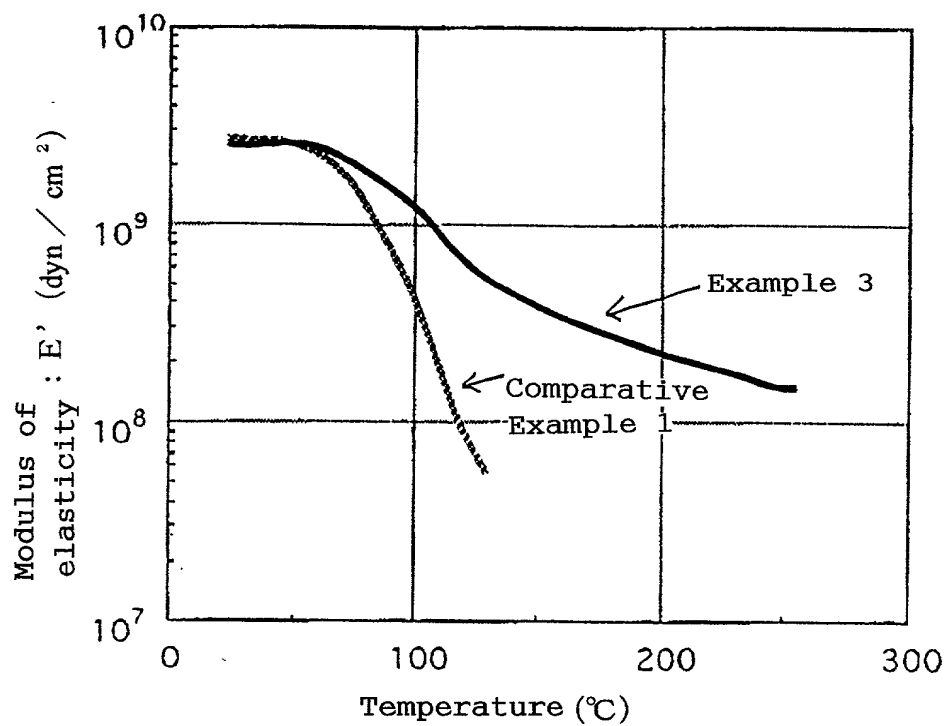


Fig. 2



# DECLARATION FOR USA PATENT APPLICATION

(including Design and National Stage PCT)

Attorney's Docket ID: \_\_\_\_\_

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below adjacent to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled MATERIAL FOR SOLID POLYELECTROLYTE SUITABLE FOR USE IN FUEL CELL

\_\_\_\_\_, the specification of which

is attached hereto. (or)

☒ was filed on May 10, 1999 [ ] and was amended on \_\_\_\_\_

[ ] as U.S. Application No. \_\_\_\_\_ (or)

[X] as International PCT Application No. PCT/JP99/02398

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 (a) - (d) or §365 (b) of any foreign application(s) for patent or inventor's certificate, or §365 (a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, where priority is not claimed, any foreign application for patent or inventor's certificate, or any PCT International application, having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s) (\_\_\_\_\_) ADDITIONAL APPLICATIONS IDENTIFIED ON ATTACHED SHEET):

Number	Country	Day/Month/Year Filed	Priority Not Claimed
<u>1998-130421</u>	<u>Japan</u>	<u>13/05/1998</u>	<u>_____</u>

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or §365(c) of any PCT International application designating the U.S., listed below; and insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application. (\_\_\_\_\_) ADDITIONAL APPLICATIONS IDENTIFIED ON ATTACHED SHEET.)

Application Serial No.	Day/Month/Year Filed	Status -- patented, pending, abandoned
------------------------	----------------------	--

I hereby appoint the practitioners of LARSON AND TAYLOR associated with the Customer Number provided below to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith, and direct that all correspondence be addressed to that Customer Number.

CUSTOMER NUMBER: 00831

Direct all telephone calls to \_\_\_\_\_, at TEL (703) 920-7200 (Fax: 703-892-8428)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full Name of Sole or First Inventor ARAKI Takayuki Citizenship Japan

Full Post Office Address c/o Yodogawa Seisakusho, DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 566-0044, Japan  
Residence - City, State/Country Same as the above  
(if different from P.O. address) JPX

SIGN AND DATE HERE: Inventor's Signature: Takayuki Araki Date: October 31, 2000

Full Name of Second Joint Inventor, if any OKA Noritoshi Citizenship Japan

Full Post Office Address c/o Yodogawa Seisakusho, DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 566-0044, Japan  
Residence - City, State/Country Same as the above  
(if different from P.O. address) JPX

SIGN AND DATE HERE: Inventor's Signature: Noritoshi Oka Date: October 31, 2000

Full Name of Third Joint Inventor, if any TANAKA Yoshito Citizenship Japan

Full Post Office Address c/o Yodogawa Seisakusho, DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 566-0044, Japan  
Residence - City, State/Country Same as the above  
(if different from P.O. address) JPX

SIGN AND DATE HERE: Inventor's Signature: Yoshito Tanaka Date: October 31, 2000

Full Name of Fourth Joint Inventor, if any NAKAMURA Takayuki Citizenship Japan

Full Post Office Address c/o Yodogawa Seisakusho, DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 566-0044, Japan  
Residence - City, State/Country Same as the above  
(if different from P.O. address) JPX

SIGN AND DATE HERE: Inventor's Signature: T. Nakamura Date: October 31, 2000

☒ SEE ATTACHED SHEET FOR SIMILAR INFORMATION AND SIGNATURE FOR ADDITIONAL JOINT INVENTORS.

Law Offices of LARSON AND TAYLOR, 727 23rd Street South, Arlington, Virginia 22202

12/96

**DECLARATION FOR USA PATENT APPLICATION**  
(including Design and PCT)

**ADDITIONAL INFORMATION SHEET**  
(use as required)

I hereby claim the benefit under Title 35, United States Code § 119 (e) of any United States **PROVISIONAL** application(s) listed below.

Application Serial No.	Day/Month/Year Filed
_____	_____
_____	_____

Additional Prior Foreign Application(s):

Number	Country	Day/Month/Year Filed	Priority Not Claimed
_____	_____	_____	_____
_____	_____	_____	_____

Additional 35 U.S.C. § 120 applications:

Application Serial No.	Day/Month/Year Filed	Status — patented, pending, abandoned
_____	_____	_____
_____	_____	_____

Additional Joint Inventors:

570  
Full Name of Fifth Joint Inventor, if any SHIMIZU Tetsuo Citizenship Japan  
Full Post Office Address c/o Yodogawa Seisakusho, DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 566-0044, Japan  
Residence - City, State/Country (if different from P.O. address) Same as the above JPX  
**SIGN AND DATE HERE: Inventor's Signature:** Tetsuo Shimizu **Date:** October 31, 2000

Full Name of Sixth Joint Inventor, if any \_\_\_\_\_ Citizenship \_\_\_\_\_  
Full Post Office Address \_\_\_\_\_  
Residence - City, State/Country (if different from P.O. address) \_\_\_\_\_  
**SIGN AND DATE HERE: Inventor's Signature:** \_\_\_\_\_ **Date:** \_\_\_\_\_

Full Name of Seventh Joint Inventor, if any \_\_\_\_\_ Citizenship \_\_\_\_\_  
Full Post Office Address \_\_\_\_\_  
Residence - City, State/Country (if different from P.O. address) \_\_\_\_\_  
**SIGN AND DATE HERE: Inventor's Signature:** \_\_\_\_\_ **Date:** \_\_\_\_\_

Full Name of Eighth Joint Inventor, if any \_\_\_\_\_ Citizenship \_\_\_\_\_  
Full Post Office Address \_\_\_\_\_  
Residence - City, State/Country (if different from P.O. address) \_\_\_\_\_  
**SIGN AND DATE HERE: Inventor's Signature:** \_\_\_\_\_ **Date:** \_\_\_\_\_